MEMORANDUM

To: EPA Region 10 Portland Harbor RI/FS File

From: Portland Harbor RI/FS Team

Date: May 2016

Subject: Evaluation of analyses used to calculate bioaccumulation calculation results
Portland Harbor Superfund Site
RAC Contract Number EP-W-05-049

PURPOSE

The purpose of this memo is to confirm the analyses used to calculate biota-sediment accumulation factors (BSAFs) and biota-sediment accumulation regressions (BSARs) presented in the Portland Harbor Bioaccumulation Modeling Report (Winward Environmental, 2015) and Appendix Da of the draft Portland Harbor Feasibility Study (Anchor QEA, 2012). The primary steps in this evaluation are:

- Review Section 4 of the Bioaccumulation Modeling Report and the current set of PRGs to identify chemicals for which confirmatory analysis is required.
- Use the results presented in Appendix A of the bioaccumulation Report, the Portland Harbor RI data base and supplemental information provided by the Lower Willamette Group (LWG) to confirm the relationship (or lack thereof) between OC normalized sediment and lipid normalized tissue.
- Determine the potential impact on the current sediment PRGs for the human health fish consumption exposure pathway (RAO 2) and ecological receptor biota (predator) exposure pathway (RAO 6).

IDENTIFICATION OF CHEMICALS

This analysis is limited to chemicals for which BSAFs or BSARs were used to develop PRGs that were used to evaluate remedial action alternatives in the Portland Harbor FS. Based on a review of Tables 2.2-5 (RAO 2 PRG Derivation) and 2.2-9 (RAO 6 PRG Derivation), the following PRGs were selected for evaluation:

- Arsenic
- Mercury

- Carcinogenic PAHs: benzo(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, dibenz(a,h)anthracene and chrysene
- Bis(2-ethylhexyl) phthalate
- Hexachlorobenzene
- Total PCBs

Human health sediment PRGs for carcinogenic PAHs, were based on consumption of shellfish. As a result, the analysis focused on benzo(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene and chrysene in field collected clams. However, the analysis also looked at the development of BSARs for benzo(a)pyrene in smallmouth bass and the development of BSAFs for benzo(a)anthracene, benzo(a)pyrene and dibenz(a,h)anthracene in large home range fish.

In addition to the above chemicals, total PCBs were included in the smallmouth bass evaluation even though PRGs were developed using the mechanistic model to determine whether a BSAR relationship could be established for total PCBs.

Because the all of the RAO 6 sediment PRGs were developed using the Arnot and Gobas mechanistic food web model, the analysis focused specifically on RAO 2 and the BSARs developed for smallmouth bass and clams and the site-wide BSAFs developed for black crappie, brown bullhead and carp. The process for identifying chemicals for evaluation is presented in Tables 1 and 2.

BSAR AND BSAF RELATIONSHIP CONFIRMATION:

BSARs were developed for those species with exposure areas smaller than the site. These species include benthic invertebrates (laboratory worms, field clams, and crayfish), sculpin, and smallmouth bass. Because PRGs were not established based on tissue-sediment relationships for benthic invertebrates and sculpin, this analysis focused on field collected clam tissue and smallmouth bass.

According to the Bioaccumulation Modeling Report, BSARs were attempted using untransformed and log-transformed sediment and tissue data as follows:

1. Untransformed tissue concentrations vs. sediment concentrations
2. Untransformed tissue concentrations vs. log-transformed sediment concentrations
3. Log-transformed tissue concentrations vs. log-transformed sediment concentrations

BSAFs were developed for large home range fish species including brown bullhead, black crappie and carp.

For organic chemicals, sediment concentrations were normalized based on OC content, and tissue chemical concentrations were normalized based on lipid content to account for the partitioning of these chemicals. No adjustments were made to sediment and tissue chemical concentrations for metals.

Field Clam BSARs:

Selected BSARs for field clams are presented in Table 4-1 of the Bioaccumulation Modeling Report. Of the 15 chemicals evaluated, relationships were established only for benzo(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene and chrysene. BSAR equations for these chemicals are presented in Table 3.

To confirm the field clam BSARs, collocated clam tissue and sediment sample data were extracted from the July 2011 version of the Portland Harbor RI data base (RI_BERA20110727+RA-SummedParams.mdb). Table 1 of Appendix A of the Bioaccumulation Modeling Report presents the collocated sediment and field collected clam tissue sample identification numbers. Sediment and tissue results were normalized to total organic carbon and total lipids respectively consistent with the procedures described in the Bioaccumulation Modeling Report. In addition, any co-located data pair with non-detected tissue or sediment concentrations was removed from the BSAR analysis, so that only pairs of detected sediment and detected tissue concentrations were used in BSAR development.

As noted in Table 4-1, all field clam BSARs were developed based on log-log relationships. According to the Bioaccumulation Modeling Report and supplemental information provided to EPA by the LWG on February 12, 2016, a correction factor was utilized when the BSARs were derived using log-transformed data. Correction factors were applied using the the “smearing estimator” of Duan (1983), as described in Helsel and Hirsh (2002). According to Helsel and Hirsh, transforming estimates from a log regression equation back into the original units imparts a bias into the BSAF estimate. Specifically, the arithmetic mean of log-data provides an estimate of the geometric mean or median rather than the arithmetic mean. The correction factor or “smearing estimator” for a linear model requires re-expressing the residuals (difference between predicted and measured or observed value) from the log-log equation into the original units, and computing their mean. This mean is the correction factor. Correction factors presented in the Bioaccumulation Modeling Report were calculated using the equation presented in Duan (1983) and the R software package. R is a software package that allows a wide range of statistical tests and analyses to be performed. The text of the R code is included as attachment A.

The results of the regression analysis confirmation as obtained from Excel (and without application of the correction factor) are presented in Figure 1. A comparison of the regression equations and r^2 values presented in Figure 1 shows that it was possible to confirm the slope of the line and the r-squared values but not the intercept due to application of the correction factor. This is significant because according to information presented in Burkard (2009), unlike untransformed data where the slope of the line is the

BSAF, for log-log transformations, the log of the BSAF is the intercept of the regression line and not the slope:

$$\ln(C(tissue)) = slope\ x \ln\big(C(sediment)\big) + \ln BSAF$$

Although calculation of the correction factor used to developed field clam BSARs has not been confirmed, application of the correction factor is consistent with the statistical procedures presented in Helsel and Hirsh. In addition, because the R software code has been provided by the LWG, sufficient documentation is available to justify the use of the field clam BSARs developed for benzo(a)anthracene, benzo(a)pyrene, benzo(k)fluroanthene and chrysene.

Smallmouth Bass BSARs:

BSARs for smallmouth bass were not established for RAO 2 PRG contaminants not included in the Food Web Model. In order to confirm the lack of a relationship, BASR relationships were attempted for arsenic, mercury, benzo(a)pyrene, bis(2-ethylhexyl) phthalate, and hexachlorobenzene. A BSAR relationship was also attempted for total PCBs to determine whether a BSAR could be developed for a chemical for which a relationship would be expected based on its physiochemical and bioaccumlative properties. Sediment SWAC data corresponding to each fish tissue sample were obtained from Appendix A of the Bioaccumulation Report. Smallmouth bass fish tissue data were taken from the July 2011 version of the Portland Harbor RI data base (RI_BERA20110727+RA-SummedParams.mdb). Whole body fish tissue (or combined fillet and body w/o fillet fractions) were lipid normalized on a sample by sample basis. Unlike the collocated clam tissue results, it does not appear that the non-detected results were eliminated from the data set prior to developing the BSARs. However, evaluation of the data with the non-detected results removed, did not improve the relationships. The results of the regression analysis are presented in Figure 2. With the exception of total PCBs, the results of the analysis confirmed the lack of a relationship between tissue and sediment. Values of r^2 for arsenic, mercury benzo(a)pyrene, bis(2-ethylhexyl)phthalate and hexachlorobenzene ranged between 0.0009 to 0.2564 depending on the transformation applied. For total PCBs, the r^2 values ranged between 0.44 and 0.50 with the untransformed data providing the best relationship. This confirms that a BSAR relationship could be developed for total PCBs.

Large Home Range Fish Tissue BSAFS:

BSAFs were calculated for large home range species. The tissue concentration was the average of available composite samples for each species, and the sediment concentration was the Study Area SWAC based on a natural neighbor interpolation. However, neither the average tissue concentrations nor the sediment SWAC results are presented in the Bioaccumulation Modeling Report.

As presented in Table 4-6, BSAFs for large home range fish species were developed for antimony, lead, benzo(a)anthracene, benzo(a)pyrene, dibenz(a,h)anthracene, tributyltin and hexachlorobenzene. However, the only chemical for which large home range fish

tissue BSAFs were used to develop RAO 2 sediment PRGs is hexachlorobenzene. A summary of the BSAFs developed is presented in Table 4.

An evaluation of the detection frequency for hexachlorobenzene in large home range fish species indicates that there were infrequent detections of hexachlorobenzene in large home range fish tissue (Table 5). Similarly, although BSAFs were developed for brown bullhead and carp for benzo(a)anthracene, benzo(a)pyrene, and dibenz(a,h)anthracene, there were no detections in 6 brown bullhead tissue samples and only 1 or 2 detections in carp samples. Although no model was developed for bis(2-ethylhexyl) phthalate, there was only one detection of this chemical in large home range fish species (brown bullhead).

Neither the Bioaccumulation Modeling Report nor the supplemental data provided by the LWG included organic carbon normalized SWACs for the chemicals of interest. As a result it is not possible to verify the BSAFs for large home range species presented in Table 4-6. However, there are limited detection of hexachlorobenzene in black crappie and brown bullhead and black crappie. The detection frequency of hexachlorobenzene in carp (9 out of 15 samples) is sufficient that this is only species for which hexachlorobenze BSAFs can reasonably be developed. The lack of detections of benzo(a)anthracene, benzo(a)pyrene, and dibenz(a,h)anthracene in large home range fish species indicates that BSAFs should not be used to develop fish consumption based PRGs for these chemicals.

SUMMARY

The results of this analysis show that a BSAR with an r^2 value of greater than 0.3 can be developed for clam tissue and the four carcinogenic PAHs evaluated, and that the slope of the line of the log-log regression can be verified. Although calculation of the correction factor has not been confirmed, the application of the correction factor is consistent with the procedures presented in Helsel and Hirsh.

The analysis also confirms the lack of a tissue sediment relationship for smallmouth bass for all chemicals that were evaluated (arsenic, benzo(a)pyrene, bis(2-ethylhexyl) phthalate, hexachlorobenzene and mercury). However, the bioaccumulation report does not present the results of the regression analysis so it is not possible to verify the BSAR equations presented in Figure 2.

The analysis also shows that with the possible exception of hexachlorobenzene in carp, there are not sufficient detections of benzo(a)anthracene, benzo(a)pyrene, and dibenzo(a,h)anthracene in large home range fish species and hexachlorobenzene in black crappie and brown bullhead to warrant the use of BSAFs to develop PRGs for these chemicals and species. However, neither the Bioaccumulation Modeling Report or the supplemental data provided by the LWG included organic carbon normalized SWACs for the chemicals of interest for which BSAFs were developed (benzo(a)anthracene, benzo(a)pyrene, dibenz(a,h)anthracene, and hexachlorobenzene).

Further, the underlying assumption BSAR in the analyses – that the BSAF should change in a linear or ln-linear fashion across all sediment concentrations – may be incorrect for some analytes and ranges of sediment and tissue concentrations. A BSAF may be applicable even when r^2 is zero (BSAF doesn't change with sediment concentration). One might still use a BSAF in this case to help guide monitoring during and after remediation.

REFERENCES:

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